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THE OXIDATION OF ALLYLIC ALCOHOLS WITH MANGANESE DIOXIDE*

By CHARLES D. ROBESON

Only a few of the oxidation methods for converting primary and secondary unsaturated alcohols to the corresponding carbonyl compounds are mild enough to be applicable to sensitive compounds. In one of these methods, manganese dioxide is utilized as the oxidant. In 1948 (1), Vitamin A was oxidized to the corresponding aldehyde when a dilute solution of the vitamin in petroleum ether was stored over solid manganese dioxide. A survey of this useful technique is worth while.

The method is simple. A solution of the alcohol in an organic solvent is brought into contact with solid manganese dioxide, usually by stirring or shaking. Filtration and evaporation of solvent give the oxidized product. By-products are few; the most common contaminant is unoxidized alcohol which can usually be separated by chromatography or distillation. In some cases, the unoxidized alcohol remains adsorbed on the oxide and is removed at the filtration step.

In a modification of the procedure, Wald (2) passed a dilute solution of Vitamin A in petroleum ether through a column of manganese oxide. Vitamin A aldehyde was recovered from the filtrate.

A number of unsaturated alcohols which have been oxidized by manganese dioxide are listed in Table I. The reaction of saturated alcohols with manganese dioxide is, with rare exceptions, too slow and incomplete to be of practical use. The list illustrates types of compounds and yields.

Factors which influence yields include:

1. *Type of Manganese Dioxide.* The kind of manganese dioxide used is important since preparations differ considerably in activity. In the present experiment, natural pyrolusite ores and some commercial products showed little activity, and other authors have reported erratic and unreproducible results with commercial oxides (3,4). Oxides prepared according to methods of Attenburrow and co-workers (5) and of Mancera and co-workers (6) are highly active and have been most frequently used, judged from published work. In this country, the General Metallic Oxides Company and the Carus Chemical Company make grades of oxide which are not as active for this purpose but are effective under properly controlled conditions.

A procedure for the oxidation of β-ionylideneethanol using one of these oxides has been reported (7).

Gritter and Wallace (8) compared the activity of manganese dioxides made by

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different procedures in the oxidation of allyl and benzyl alcohols and concluded that the dioxides prepared with permanganate or chromate were the most active. These authors confirmed earlier statements of Henbest (9) and Evans (10) that the activity is influenced by the degree of hydration of the oxide. Thus, careful control in preparing and drying the oxide is needed to ensure consistent activity.

Weedon and Woods (11) proposed the oxidation of cinnamyl alcohol under standardized conditions to screen commercial manganese dioxide preparations for use. This method was used in studies by Bharucha (12).

Only a part of the oxygen in manganese dioxide is available in these oxidations. Hence, the amount of oxide used is usually five to fifteen times (by weight) that of the compound being oxidized. Henbest and Thomas (9) have indicated that the amount of oxygen available for a given weight of oxide varies with the chemical nature of the substrate. For example, a larger quantity of oxide is needed to oxidize allylic alcohols than is needed to oxidize quinols.

2. *Solvents.* The solvent used in the oxidation of allylic alcohols can usually be varied, although, in certain cases, one may give the maximum yield. Solvents used include petroleum ether, naphtha benzene, acetone, chloroform, dichloroethane, and carbon tetrachloride. When using highly active oxide preparations, chlorinated solvents are recommended, since ignition of the vapors of flammable solvents has been reported (3).

The amount of solvent is not critical; amounts from five to ten times the volume of alcohol being oxidized are commonly used. Some workers have employed as much as one hundred volumes (13).

3. *Time and Temperature.* The time and temperature required depend on the quantity and activity of the manganese dioxide. Most reported oxidations have been carried out at room temperature. Attenburrow (5) has emphasized the shorter reaction time required with his "active" oxide. Gritter and Wallace (8) determined the time needed for maximum yield for different preparations.

In the experiments with β-ionylideneethanol, the optimum reaction time has varied from about 2 hr. for material prepared by the Attenburrow procedure to 16 hr. for some commercial oxides. Longer contact times are not, in general, harmful. The progress of the reaction can be followed by the change in ultraviolet absorption, since the conversion of hydroxyl group to carbonyl shifts the absorption maximum to a longer wavelength.

Mechanism

Oxidation appears to proceed by adsorption of the alcohol on the surface of the oxide followed by desorption after oxidation, but little else is known about the mechanism.

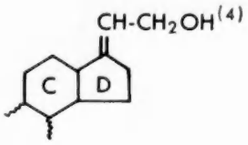
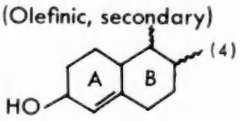
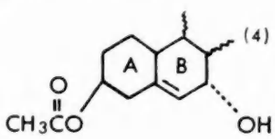
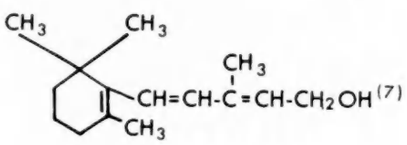
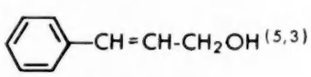
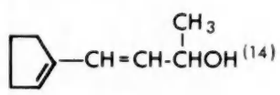
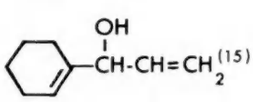
Harfenist and co-workers (3) have suggested that some oxidations stop when the amount of carbonyl compound reaches a critical value, presumably representing a concentration at which the carbonyl compound displaces the alcohol from the oxide surface.

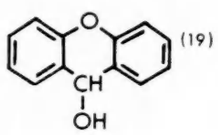
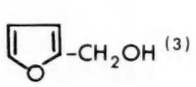
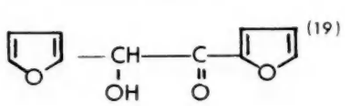
These authors also discussed the relation between oxidation potential and ease of oxidation. Their suggestion that steric effects may be important was demonstrated by Rapoport (14) who showed that *cis*-10-hydroxydihydrodesoxycodeine is more readily oxidized than the *trans*-alcohol.

Other Oxidations

Manganese dioxide oxidizes other compounds besides allylic alcohols. It oxidizes 2-hydroxytetrahydropyran to γ-valerolactone (18), N-alkylamines to N-formyl-

TABLE I

Alcohol	Yield, %
(Olefinic, primary)	
$CH_2=CH-CH_2OH$ [5,8]	57, 100
$CH_3-C(CH_3)=CH-CH_2CH_2-C(CH_3)=CH-CH_2OH$ [3]	79
 [4]	> 90
(Olefinic, secondary)	
 [4]	> 90
 [4]	> 90
 [7]	95
 [5,3]	75, 77
(Polyenic, secondary)	
 [14]	50
 [15]	90
$C_6H_5-CH(OH)-CH=CH-CH_3$ [12]	70
$C_6H_5-CH=CH-C(CH_3)=CH-CH=CH-CHOH(CH_3)$ [11]	77
(Primary, acetylenic)	
$R-[C\equiv C]_2-CH=CH-CH_2OH$ [16]	"High"
(R = $CH_3CH_2CH_2-$, $CH_3CH=CH-$, R-C≡C-)	

Alcohol	Yield, %
(Secondary, acetylenic)	
$CH_3CH_2CH_2CH_2-C\equiv C-CH(OH)-CH_3$ [5]	Quantitative
$C_6H_5-CH(OH)-C\equiv C-CH_3$ [12]	80
$HC\equiv C-CH=CH-CH=CH-CH(OH)-CH_3$ [17]	80
(Aromatic, primary)	
$C_6H_5CH_2OH$ [3,18]	80, 89
$C_6H_5CH_2OH$ (p-substituted) [3]	70-80
(Aromatic, secondary)	
$C_6H_5CH_2CH_2-CH(OH)-C_6H_5$ [19]	50
 [19]	100
$C_6H_5CH(OH)-C_6H_5$	33
(Heterocyclic, primary)	
 [3]	69
(Heterocyclic, secondary)	
 [19]	88

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amines or to the amine and the corresponding aldehyde (9), aliphatic alcohols to aldehydes or ketones (20), and allylic methylene groups to hydroxylic or ketonic groups (21). The reaction conditions are often as mild as for the allylic alcohols.

An excellent review article by Evans embracing a broader coverage of the general subject of manganese dioxide oxidations has recently appeared (22) and presents a convenient source of additional information.

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